ESR CENTERS AND CHARGE DEFECTS NEAR THE SILICON/SILICON DIOXIDE INTERFACE

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return it to the originator.
The Nishi-B ESR center has been examined as a function of thermal oxidation and annealing conditions in single-crystal silicon wafers. It was observed that B concentration was not correlated with fixed surface-state charge density $Q$, despite some similarities in their behavior. In freshly oxidized wafers, B typically ranges up to 200 per $\text{nm}^2$, and $Q$ up to 50 per $\text{nm}^2$. The concentration of B is highly dependent on cooling rates; concentration does not depend on oxide thickness and B may be observed even in native oxides. The $g$-value of the orientation-averaged B signal (2.0064) favors its assignment to trivalent Si.
20. Abstract (cont'd)

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CONTENTS

INTRODUCTION 1

EXPERIMENTAL DETAILS 1

RESULTS AND DISCUSSION 2

Character of Esr Signals 2

Identification of Centers 2

Relation to Interface Charge Defects 3

REFERENCES 5

FIGURES

1. $P_b$ signal from $[\overline{1}11]$ silicon (a) one trace (b) 400 traces. 2
2. $P_b$ signal from $[100]$ silicon (a) $H_{\parallel}[100]$ face (b) $H_{\parallel}[110]$. 2
3. $g$-anisotropy for $P_b$ $[\overline{1}11]$, rotation plane (a) $[11\overline{2}]$ (b) $[\overline{1}10]$. 3
4. $P_b$ signal vs $Q_{ss}$ on $[\overline{1}11]$ (a) p-Si (b) n-Si. 4

TABLES

1. $P_b$ vs cooling rate. 4
2. $P_b$ vs oxide thickness. 4
ESR CENTERS AND CHARGE DEFECTS NEAR THE Si/SiO₂ INTERFACE

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ABSTRACT

The esr center P_b has been examined as a function of thermal oxidation and annealing conditions in single-crystal silicon wafers. It was observed that P_b concentration was not correlated with fixed surface-state charge density Q_ss, despite some similarities in their behavior. In freshly oxidized wafers, P_b typically ranges up to 2x10¹² cm⁻², and Q_ss up to 5x10¹¹ cm⁻². The concentration of P_b is highly dependent on cooling rates; concentration does not depend on oxide thickness and P_b may be observed even in native oxides. The g-value of the orientation-averaged P_b signal (2.0064) favors its assignment to Si⁺⁺⁺⁺ in a silicon environment, as in crushed silicon (2.0055), rather than to the well-studied E' centers (2.0008) found in various forms of damaged SiO₂. In our thermal oxides, E' centers were unobservable, and thus cannot be the main source of Q_ss, despite their nominal positive charge. Preliminary evidence shows a correlation of P_b with initial, unannealed "fast" interface states N_st, supporting the idea that Si⁺⁺⁺⁺ is the origin of these states.

INTRODUCTION

High-performance integrated circuit devices are required for a variety of advanced military electronic systems. The performance and reliability of these devices can be unacceptably degraded by the presence of certain atomic-scale defects near the Si/SiO₂ interface, which can cause noise, loss of gain, bias drifts, and ultimate failure. Diagnosis and control of these defects is essential as IC devices move into the submicron regime.

Extensive studies of the Si/SiO₂ interface by electrical methods have not defined the origins of interface defects (1). The wealth of esr studies of silicon, quartz, and glass suggests application of esr to the interface. Nishi (2) observed and tentatively identified three main esr signals from thermally oxidized silicon wafers, P_a, P_b, P_c. The P_b signal, visible at 300 K (3), seems to have the greatest significance for the defect structure of the Si/SiO₂ interface. Our study was prompted by Nishi's tentative identification of P_b with the E' centers of damaged silica, and by the implied connection between P_b and surface charge Q_ss evidenced by similar depth profiles. We have attempted to confirm these conclusions or offer alternatives.

EXPERIMENTAL DETAILS

The samples were from n- and p-type Monsanto double-polished wafers, 100-300 ohm-cm. They were cleaned and oxidized in a quartz-tube diffusion furnace by standard semiconductor procedures. For C-V measurements, one-micron aluminum was evaporated onto the etched or sandblasted back surface and 1.2 mm dots were evaporated onto the oxide. A PAR system was used at 1.0 MHz. Samples consisted of 4 to 6 pieces 4x20 mm, with [111] or [100] face. A Varian 4501 with dual cavity was used for spin concentration, and an E-line Century for anisotropy and line structure. An H-P 5480 signal averager was used. All runs were at 300 K.
RESULTS AND DISCUSSION

Character of ESR Signals

Samples with \{111\} face showed \(P_b[111]\) signals with up to 20:1 signal-noise without averaging. A typical \(P_b[111]\) signal is shown in Fig. 1a. The line shows reproducible structure which is symmetrical about the center, and is superimposed on a wider low-amplitude signal which contributes to an anisotropic asymmetry of the line base. This latter signal is mostly residual silicon damage at \(g=2.0055\). In Fig. 1b, the signal has been accumulated 400 times; much detail is seen, nearly all from the silicon. Hoped-for symmetrical hyperfine lines are not evident in the clutter, with the possible exception of the close-in blips noted above.

![Fig. 1. \(P_b\) signal from \{111\} silicon (a) one trace (b) 400 traces.](image)

Signals from the \{100\} face are different (Fig. 2). The s-n ratio is much worse than \(P_b[111]\) signals; 16 to 64 traces were used. The line has several ill-defined components, with narrowest, least-structured appearance at \(25^\circ-30^\circ\) from \{100\} face axis. Resolution is impossible at this time.

![Fig. 2. \(P_b\) signal from \{100\} silicon (a) \(H_{o\perp}[100]\) face (b) \(H_{o\perp}[110]\).](image)

Anisotropy of \(P_b[111]\) is well confirmed in our studies. Within errors, our signal shows \{111\} axial symmetry, \(g_H=2.0013, g_A=2.0081\). The \(g\)-map is shown in Fig. 3. Only one limb is observed, for spin centers with major axis normal to the interface. The line width of \(P_b[111]\) varies from 1 G on \{111\} to 3 G at 90\(^\circ\). For \(P_b[100]\) (not shown) one possible but arbitrary deconvolution gives 2 components with \(g\)-anisotropy like \(P_b[111]\).

Identification of Centers

The anisotropy and \(g\)-values of \(P_b[111]\) are like other centers observed in
irradiated silicon (4-6) which have been ascribed to Si^{III} with unbound orbital facing into a vacancy. In a study of the Si-E center (vacancy plus phosphorus), Watkins and Corbett (5) calculate the anisotropy for a Si^{III} fragment ($\Delta g_n$ = 0; $\Delta g_{l_\perp}$ = 0.017). They ascribe the deficiency vis-a-vis observed values ($g_1$ = 2.0005, $g_2$ = 2.0112, $g_3$ = 2.0096) to delocalization, and the hfs is consistent. Other well-characterized centers having similar anisotropy are the negatively-charged divacancy (G-7) (6), and the low-temperature form of the five-vacancy cluster (4). In view of the similarity of Pb[111] to these Si^{III} defects, we assign it to Si^{III} bonded to silicon, not oxygen, with unpaired p-rich orbital normal to the interface. The variation in line width may reflect different g-values in different sites.

Pb[111] is not like the E' center of damaged quartz (7-8), which has a lower $g_{av}$ and much weaker, prolate anisotropy ($g_1$ = 2.0018, $g_2$ = 2.0005, $g_3$ = 2.0003).

The identification of Pb[100] is not clear at present. We have been unable to resolve its map into combinations of single Si^{III} signals or bent-bond signals (like the Si-Bi center, structurally plausible for the [100] face).

Relation to Interface Charge Defects

It is well known that $Q_{SS}$ in thermal oxides is controlled by the final annealing temperatures (Deal triangle) (1). Figure 4 shows a series of p- and n-type samples grown at 1000 C in dry O$_2$, but annealed for an hour in O$_2$ at various temperatures. For both p and n, $Q_{SS}$ values were found to follow the trend of the Deal triangle; the magnitude of Pb[111] did not. This is contrary to our first tests, where correlation existed between Pb and $Q_{SS}$ (9). (Earlier samples were erratically cooled.)

The values of $Q_{SS}$ increase with longer cooling time (1). Table I shows the variation of Pb[111] with cooling rate. After oxide growth, one sample was given the standard fast pull, and the other was cooled slowly in situ by turning off the furnace, while the oxygen continued to flow. Also compared are two samples annealed one hour in N$_2$ after oxidation, and respectively slow- and fast-cooled in N$_2$. The Pb results are different from $Q_{SS}$. The sample slow-cooled in O$_2$ had $Q_{SS}$ about three times higher than the other samples, as expected. But the Pb signal is lower in the slow-cooled samples, whether the oxidation is followed by a nitrogen anneal or not. Nishi (2)
likewise observed that faster quenches generally enhanced $P_b$ signals. 

![Diagram](image)

Oxygen Annealing Temperature, C

Fig. 4. $P_b$ signal vs $Q_{ss}$ on [111] (a) p-Si (b) n-Si.

The dependence of $P_b$ [111] centers on grown-oxide thickness reflects their site and origin. The spin concentrations shown in Table II are constant over two orders of magnitude in thickness. Moreover, we have recently observed $P_b$ with nitrogen-annealed native oxides. Our results disagree with Nishi's report [2] of large increase in $P_b$ from 2000 Å to 4000 Å, and are inconsistent with the depth profile obtained by etching [2], which peaks at $>150$ Å. Constant $P_b$ suggests association with the immediate interface region only.

A seemingly oxide-located signal might come from small islands of silicon in the oxide or from centers in the silicon surface whose paramagnetism disappears when the last remnants of the oxide overburden are removed. A stress-related center would behave in the latter fashion [10]. $Si_{III}$ with unpaired orbital directed perpendicular to the interface is much more reasonable chemically than preferential $Si_{III}$ orientation far out in the oxide. In this view, neither $P_b$ centers nor unobserved $E'$ centers are the major source of $Q_{ss}$. (Quasi-$E'$ centers—a doubly-charged pair of $Si_{III}$, or isolated singly-charged $Si$, invisible to esr—are not ruled out.)

<table>
<thead>
<tr>
<th>Table I. $P_b$ vs cooling rate.</th>
<th>Table II. $P_b$ vs oxide thickness.</th>
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<tbody>
<tr>
<td>Cooling Conditions</td>
<td>$Q_{ss}$ (Rel.)</td>
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<tr>
<td>$O_2$ fast cool</td>
<td>3.5</td>
</tr>
<tr>
<td>$O_2$ slow cool</td>
<td>11.</td>
</tr>
<tr>
<td>$N_2$ fast cool</td>
<td>3.5</td>
</tr>
<tr>
<td>$N_2$ slow cool</td>
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Lack of correlation of $P_b$ and $Q_{ss}$ must be viewed in respect to usual device processing regimens. Determination of $Q_{ss}$ is assumed to be made after aluminum dot deposition and annealing—this reduces $N_{st}$ (1) and allows a tractable C-V plot of the presumably unaffected fixed charge. The concentration of interface states $N_{st}$ in freshly oxidized wafers is of the same order as
$P_b$, $10^{12}$ cm$^{-2}$. Esr spectra, however, are taken on wafers which have not been "annealed." We prepared a sample with substantial $P_b$ signal, deposited aluminum over the sample surface, and "annealed" it. After removing the aluminum, there was no detectable esr. Nishi (2) has noted that water vapor during oxidation affects $P_b$ and $N_{st}$ similarly. Finally, weaker $P_b$ signals on [100] faces correlate with lower $N_{st}$ values typical of [100] wafers.

In summary, we believe that the $P_b[111]$ signal arises from $Si^{III}$ at the interface, and that it is not the source of $Q_{ss}$. Furthermore, silica $E'$ centers, not observed by esr in oxidized wafers, are likewise not a major source of $Q_{ss}$. Presently, the observed evidence favors a closer relation between $P_b$ and $N_{st}$ than between $P_b$ and $Q_{ss}$. If substantiated, this would help to confirm the concept that $Si^{III}$ is a source of initial interface states.

REFERENCES


